Beryllium 9110

by Field-Portable Fluorescence Measurement

Be | MW: 9.0121 | CAS: 7440-41-7 | RTECS: DS175000

METHOD: 9110, Issue 1	**EVALUATION: PARTIAL**	**Issue 1: DRAFT**

OSHA : No PEL	**PROPERTIES:** solid; d 1.85 g/ml; MP 1278°C; VP 0 kPa (0 mm Hg) @ 25 ˚C
NIOSH: No REL	
ACGIH: No TLV	

SYNONYMS: Beryllium metal

SAMPLING		MEASUREMENT	
SAMPLER:	WIPE (cellulosic)	**TECHNIQUE:**	Field-portable fluorescence measurement
FLOW RATE:	N/A	**ANALYTE:**	Complex of Hydroxy benzoquinoline sulfonate (HBQS) with beryllium
VOL-MIN:	N/A		
-MAX:		**SAMPLE DISSOLUTION:**	1% ammonium bifluoride (aqueous)
SHIPMENT:	Routine	**DETECTION SOLUTION:**	63.4 μM HBQS / 2.5 mM EDTA / 50.8 mM lysine monohydrochloride (pH adjusted to 12.85 with 10 M NaOH)
SAMPLE STABILITY:	Stable	**EXCITATION λ:**	380 nm
BLANKS:	2 to 10 field blanks	**Detection λ range**; λ_{max}:	400 – 700 nm; 475 nm

ACCURACY		
RANGE STUDIED: 0.02 to 12.0 µg/wipe	**CALIBRATION:**	Elemental beryllium in detection solution
BIAS: none identified	**RANGE:**	0.06 to 6 µg/wipe
OVERALL PRECISION ($\hat{S}_{rT}$): 0.057	**ESTIMATED LOD:**	0.02 µg/wipe
ACCURACY: 11.6 (6.4 – 16.8, 95% C.I.)	**PRECISION ($_r$):**	0.021 @ ~0.2 µg/wipe (n = 15); 0.076 @ ~1.5 µg/wipe (n = 6); 0.052 @ ~3µg/filter (n = 6)

APPLICABILITY: The working range of the method is 0.02 to 6.0 µg/100 cm^2 for surface wipe samples. The analysis is for total beryllium and is not compound specific.

INTERFERENCES: Minor interference (<10%) from Fe can result if iron concentrations are high. Samples high in iron demonstrate a yellow or gold coloration. This interference can be minimized by allowing the solution to sit for at least four hours, during which time the solution clears and then filtering the sample extract before use,

OTHER METHODS: Method 7300 (hot plate or microwave digestion and inductively coupled plasma atomic emission spectrometry) is an alternative (reference) procedure for the determination of elemental beryllium. ASTM method D7202-05 is a similar procedure to detect elemental beryllium by fluorescence.

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REAGENTS:

1. Dissolution solution: 1% Ammonium bifluoride (prepared from dissolving 1g ammonium bifluoride in 100ml of deionized water).
2. Detection solution: 63.4 μM hydroxyl benzoquinoline sulfonate (HBQS) [1] / 2.5 mM ethylene diamine tetraacetic acid (EDTA) / 50.8 mM lysine monohydrochloride (pH adjusted to 12.85 with 10 M NaOH).
3. Water, deionized.
4. Beryllium spectroscopic standard solution, ~1,000 μg/ml (commercially available).
5. Spiked beryllium media (commercially available)

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Wipe material, cellulosic, 47-mm minimum diameter, wetted
   NOTE: Polyvinyl alcohol (PVA) media are unsuitable for this method.
2. Templates, disposable reusable, 100 cm^2 minimum area
3. Tape, masking
4. Portable ultraviolet/visible (UV/Vis) fluorometer, with irradiance excitation lamp (λ = 380 nm) and time-integrating visible detector (400 – 700 nm, $\lambda_{max} \approx 475$ nm)
5. Mechanical agitator, shaker or rotator
6. Fluorescence cuvettes, disposable, 10-mm diameter, transparent to UV/Vis radiation
7. Centrifuge tubes, plastic, 15-ml
8. Syringe filters, 0.45-μm nylon, 13- or 25-mm diameter, in plastic housings.
   NOTE: Polytetrafluoroethylene (PTFE) filters are unsuitable for this method.
9. Pipettors, mechanical, of assorted sizes as needed
10. Pipet tips, plastic, disposable, of assorted sizes as needed
11. Labware, plastic (e.g., beakers, flasks,

graduated cylinders, etc.), of assorted sizes as needed

12. Tweezers, plastic or plastic-coated
13. Laboratory wipes
14. Personal protective wear, e.g., respirators, masks, gloves, lab coats, safety eyewear, etc. as needed

SPECIAL PRECAUTIONS: Wear appropriate personal protection during sampling activities and analysis. Perform sample preparation and analysis in a clean well ventilated area that is well removed from any possible beryllium contamination. It is ESSENTIAL that suitable personal protective equipment, including suitable gloves, eye protection, laboratory coat, etc. is used when working with the chemicals. Any area affected by the detection or dissolution solution must be immediately washed with plenty of water. Ammonium bifluoride will etch glass, so it is essential that all NH_4HF_2 solutions are contained in plastic labware. Avoid exposure by contact with the skin or eyes, or by inhalation of the vapor.

SAMPLING:

1. Don a clean pair of gloves.
2. Demarcate the sampling area (100 cm^2 minimum) using a clean template or tape. If a template is used, tape the outside edges of the template to the surface to prevent its moving during sampling.

3. Using a clean wipe, sample the demarcated area using the procedure described in ASTM D6966 [2].
4. Place each wipe sample into labeled 15-ml plastic centrifuge tubes.

SAMPLE PREPARATION:

5. Add 5 ml of the dissolution solution (1% ammonium bifluoride) to each 15-ml centrifuge tube containing surface swipe sample, and cap each tube.
6. Place each tube into a mechanical rotator, and rotate for at least 30 min.

   NOTE: Rotator may also be substituted by a shaker or an agitator as long as the dissolution solution wets the wipe well. Sonication has also been shown to be effective. Dissolution of refractory material such as beryllium oxide by heating the solution to 80°C for 30 minutes without agitation has been shown to be effective.
7. Into clean beakers, flasks, or tubes, filter each solution with a nylon syringe filter.
8. Into cuvettes containing 1.9 ml of detection solution, pipet 0.1 ml of each sample filtrate. Cap and mix briefly.

   NOTE: If high iron or titanium concentration is suspected or is evident (owing to the appearance of suspended precipitate), allow the solution to settle, or filter the solution using a nylon syringe filter.

   NOTE: The stability of the detection and the dissolution solution is more than one year and of the mixed measurement solution comprising both is greater than 30 days. The solutions must be kept in sealed containers and the detection and mixed solutions must be stored away from light.

   NOTE: Alternative ratios of dissolution solution comprising beryllium and detection solution may be used for analyzing alternative range of beryllium concentration.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate the fluorometer according to the manufacturer’s recommendations.

   NOTE: Beryllium stock standard solutions are made up using Beryllium spectrometric standards diluted into 1% ammonium bifluoride. Calibration check standards are then prepared by adding 0.1 ml of beryllium stock standards into 1.9 ml of detection solution (20-fold dilution). A recommended series of standard stock solutions are 800 ppb, 200 ppb, 40 ppb, 10 ppb and 0 ppb to measure a range of 0.2 µg to 4 µg of beryllium on the sampling media.

NOTE: If alternative ratios of dissolution solution comprising beryllium and detection solution are used for sample preparation, then a similar ratio for calibration is required.

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10. Analyze a calibration standard, a reagent blank, and a media blank at least once every 20 samples. Ensure that the concentration range of the calibration standards spans the measured beryllium levels in the samples.
11. Check recoveries with at least two media spikes per ten samples.

    NOTE: It is recommended to use beryllium oxide (BeO) for media spikes.

MEASUREMENT:

12. For each sample, obtain the fluorescence spectrum using a 380-nm excitation lamp and visible (400-700 nm) detector (follow instrument manufacturer's instructions).
13. If the fluorescence values for any of the samples are above the range of the calibration standards, dilute the solutions with detection solution, reanalyze, and apply the appropriate dilution factor in subsequent calculations.

CALCULATIONS:

14. Obtain the solution concentration for each sample, C_s (µg/l), and the average media blank, C_b (µg/l).
15. Using the solution volumes of sample, V_s (ml), and media blank, V_b (ml), calculate the concentration, C (µg/100 cm^2) of Be in the sample of area A, while accounting for the dilution factor DF. The calculations below give the amount of beryllium in the wipe. It is assumed that 100 cm^2 area was wiped to collect the sample. If the area wiped is different from this number then the calculations need to be adjusted so that the results are normalized to 100 cm^2 area.

$$C = DF \times \frac{\left[C_s\ V_s - C_b\ V_b\right]}{A}, \mu g/100cm^2$$

NOTE: The table below can be used for correlating the amount of beryllium in the solution to the beryllium in the sampling media.

Preparation of Standard Solutions	**Final concentration of beryllium (ppb) in calibration standard solutions**	**Corresponding amount of beryllium in the media***
0.1 ml of **0 ppb standard** + 1.9 ml of detection solution	0.0	Corresponds to 0.00 µg Be on media
0.1 ml of **10 ppb standard** + 1.9 ml of detection solution	0.5	Corresponds to 0.05 µg Be on media
0.1 ml of **40 ppb standard** + 1.9 ml of detection solution	2.0	Corresponds to 0.2 µg Be on media
0.1 ml of **200 ppb standard** + 1.9 ml of detection solution	10.0	Corresponds to 1 µg Be on media
0.1 ml of **800 ppb standard** + 1.9 ml of detection solution	40.0	Corresponds to 4 µg Be on media

*Incorporating sample dilution factor for 5 ml of dissolution solution; note that volumes other than 5 ml will require a different appropriate dilution factor.

EVALUATION OF METHOD:

The method was evaluated in accordance with published guidelines [3]. Experiments were conducted using an Ocean Optics® portable fluorescence device with the following components:

USB 200 spectrometer with spectral grating #2 (UV/Vis 600)

LS-1 lamp (380-nm) in LS-450 housing

UV-2 casting
OFLV linear filter 200-850
L2 collection lens and slit-200

Tests were carried out in relative irradiance mode using 2- or 5-sec integration times.

The method was evaluated using beryllium oxide spiked onto Whatman #541 cellulose and nylon filters at levels of 0, 0.02, 0.1, 0.2, 0.3, 0.4, 1.5, 3.0, and 6.0 µg (five samples at each level).

The method was also field-tested using real-world samples (collected using Whatman #541 cellulose and nylon filters) obtained at U.S. Department of Energy sites suspected to be contaminated with beryllium. Field samples measured by portable fluorometry were also analyzed using hot plate digestion and ICP-AES analysis; the latter served as a reference analytical method. Sample loadings observed ranged from below detection limit (<0.02 µg/sample) to ~12 µg/sample.

Long-term stability of samples was verified from spikes (n = 30) of 0.1 µg Be on Whatman #541 cellulose and nylon filters. Samples were analyzed at day one (n = 12) and then one week (n = 6), ten days (n = 3), two weeks (n = 3), three weeks (n = 3), and one month (n = 3) after spiking. No diminution of fluorescence signal was observed from samples prepared and analyzed after having been stored for up to thirty days.

Interference tests were carried out using solutions of 0 nM, 100 nM, and 1.0 µM Be in the presence of 0.4 mM Al, Ca, Co, Cu, Fe, Ti, Li, Ni, Pb, Sn, U, V, W, and Zn (separate experiments were carried out for each potential interferant).

REFERENCES:

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[2] ASTM D6966 (2003), Standard Practice for Collection of Surface Wipe Samples for Subsequent Determination of Metals. American Society for Testing and Materials (ASTM): West Conshohocken, PA.

[3] Kennedy ER, Fischbach TJ, Song R, Eller PM, Shulman SA (1995), Guidelines for Air Sampling and Analytical Method Development and Evaluation. CDC/NIOSH: Cincinnati, OH; DHHS (NIOSH) Publ. No. 95-117.

[4] Minogue EM, Ehler DS, Burrell AK, McCleskey TM, Taylor TP [2005]: Development of a new fluorescence method for the detection of beryllium on surfaces. J. ASTM Int. **2**(9), 10 pp.; Paper ID JAI13168..

[5] Ashley K, McCleskey TM, Brisson MJ, Goodyear G, Cronin J, Agrawal A [2005]: Interlaboratory evaluation of a portable fluorescence method for the measurement of trace beryllium in the workplace. J. ASTM Int. **2**(9), 8 pp.; Paper ID JAI13156.

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